

LETTERS TO THE EDITOR.

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The Spectrum of Krypton.

PROF. RUNGE, in your last issue, points out that the wave-length of the bright green line of krypton is 5570.4 (Rowland's scale), while that of the auroral line is about 5571. In the paper presented to the Royal Society by Dr. Travers and myself on June 3, the wave-length is given as 5567.7. The wave-length was re-measured by Mr. Baly on June 7, and its value was found to be 5570.0. That of the feebler green was 5561.8, and of D₄, the yellow line, 5870.0. These values, read by means of a grating, are very close to those given by Prof. Runge. We hope to publish photographic measurements of the other lines shortly.

WILLIAM RAMSAY.

University College, London, November 15.

Stereochemistry and Vitalism.

ALTHOUGH Prof. Japp has already replied to the criticisms which have appeared in NATURE on his address to the Chemical Section of the British Association, we should be glad, in view of the interest taken in the matter, and also because we have been investigating externally compensated and optically active compounds for some years past, if you could find space in which we may continue the discussion and bring forward a few facts in support of our views.

In the first place, we will briefly summarise the main points on which there seems to be general agreement, as follows:—Compounds, optically inactive by external compensation, can be prepared under symmetric conditions—such compounds, under suitable and symmetric conditions may separate from solution in enantiomorphously related crystals; under symmetric conditions crystals of the two enantiomorphs are deposited in equal numbers, and the crystalline deposit as a whole, as well as the mother liquor, if separated, are both optically inactive.

Now Prof. Japp contended that, in order to obtain an optically active deposit or mother liquor from such an externally compensated compound (without the aid of some pre-existing asymmetric influence), an intelligently selective or vital force must be called into action, and consequently that vitalism determined the existence of optically active compounds in nature; in his reply he modifies his original contention by introducing the word "constantly"; but this modification makes very little, if any, difference to the arguments which we adduce. His critics, on the other hand, have attempted to show, with what success we do not venture to express an opinion, that chance alone, or other causes apart from vitalism, may have brought about the present occurrence of enantiomorphous compounds in organised nature.

Having frequently had occasion to study the spontaneous crystallisation of externally compensated substances, we had in mind various observations, especially some made during recent work, which led us, from the first, to doubt the validity of Prof. Japp's views. Let us consider, in the first instance, the case of sodium chlorate, a substance which separates from solution in enantiomorphously related crystals. On allowing saturated solutions of this salt to crystallise spontaneously, we found that in only two experiments out of forty-six were equal numbers of dextro- and laevo-rotatory crystals deposited (*Trans. Chem. Soc.*, 1898, 606), the percentage of dextro-rotatory crystals in the 46 crops varying from 24.14 to 77.36; nevertheless, the weighted mean percentage of dextro-rotatory crystals obtained was 50.08 ± 0.11. It is obvious, therefore, that on crystallising this substance under symmetric conditions equal numbers of dextro- and laevo-rotatory crystals are finally obtained, and yet in a single deposit one or other form may be present in large excess.

On the publication of Prof. Japp's address, we hastened to obtain further experimental evidence bearing on this point. For this purpose a saturated solution of sodium chlorate was allowed to evaporate spontaneously, three unselected crystals of the salt of unknown rotation being introduced as nuclei; after a week's time each of the three crystals had grown to a large size, and was very well developed. One of these, weighing 47 grams, was removed from the solution and broken into small

pieces which were seeded into saturated solutions of the chlorate; the latter were then placed aside to crystallise. After a week's time these solutions were full of well-developed crystals, which were removed and examined; the crystals were 269 in number, and were all dextro-rotatory.

This experiment shows that an enantiomorphous system may originate from a non-enantiomorphous one without the introduction of any intelligently directive or enantiomorphous influence, and under conditions which might well arise in an inorganic non-enantiomorphous universe. This being so, it is illogical to assume in the present rudimentary state of our knowledge of the subject that enantiomorphism of this kind could not cause enantiomorphism in a system containing a substance such as racemic acid or some other externally compensated compound.

Now, although a solution of sodium chlorate deposits on the average equal numbers of dextro- and laevo-rotatory crystals, this does not preclude the possibility of other similar compounds which separate from solution in enantiomorphously related crystals giving a preponderance of one or other form, owing possibly to enantiomorphous influences exerted by surrounding conditions, such, for example, as the earth's enantiomorphism; in fact, as we have already pointed out (*Trans. Chem. Soc.*, 1898, 611), observations in support of this view are not lacking, although they require, and are now receiving, further examination.

We have also shown (*Proc. Chem. Soc.*, 1898, 113) that, apparently, a close analogy exists between the behaviour of sodium chlorate and of an externally compensated mixture of dextro- and laevo-rotatory sodium ammonium tartrates; this parallel we are at present investigating. The first step in our examination of sodium chlorate was to ascertain the ratio between the numbers of dextro- and laevo-rotatory crystals deposited from solution, with the results briefly summarised above; obviously a similar step is necessary in the case of the mixed tartrates. The results which have been obtained in these experiments contrast remarkably with those recorded in the case of sodium chlorate, and are absolutely at variance with the views expressed by Prof. Japp. Ten such solutions have so far been examined, and in every case a strongly dextro-rotatory deposit was obtained, the mother liquor, of course, being strongly laevo-rotatory. We put these experimental results forward with considerable reservation as the work is not complete and we may discover some disturbing influence; but, inasmuch as attention has of late been concentrated on this fascinating subject by Prof. Japp's equally fascinating presentation of it, we feel compelled to make this short statement of the results up to the present obtained in developing the work which we have in hand.

Much more might be written with a view to suggesting the possible sequence of events which might have led to the present conditions of organised nature, but it is of little use attempting such a task until a great deal more experimental evidence is before us.

F. STANLEY KIPPING.

WILLIAM J. POPE.

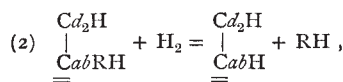
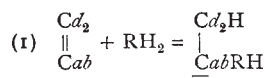
THE following seems to me a perfectly possible, although purely hypothetical, way in which any amount of an optically active compound could be formed by chance chemical processes.

Let an admixture of chemical compounds be such that only one molecule of an optically active compound is formed. Or, if you like, let a volcanic explosion scatter a collection of equal quantities of dextro and laevo molecules in such a way that one molecule only falls in a certain pool of water containing inactive bodies in solution.

This single molecule must be either dextro or laevo. Let us suppose it is a dextro molecule.

Furthermore, let it be of such a nature that it can react catalytically with surrounding molecules in such a way as to produce in these an asymmetric atom:

e.g.



where *abcd* are any monovalent radical not containing an asymmetric carbon atom, while R is a dextro-rotatory bivalent radical. The first molecule formed, according to equation (1), will have the underlined C dextro or laevo, being determined by R being dextro.

When this decomposes according to equation (2) the C will still be active, and one active molecule of $\begin{array}{c} \text{Ca}_2\text{H} \\ | \\ \text{CabH} \end{array}$ will have been produced.

But RH_2 is reproduced, and is consequently capable of repeating this action indefinitely, and of making an indefinite number of $\begin{array}{c} \text{Ca}_2\text{H} \\ | \\ \text{CabH} \end{array}$ molecules with activity of the same sign.

Furthermore, this action is scarcely to be distinguished in principle from the reactions brought about by unorganised ferments or enzymes.

W. M. STRONG.

Helstonleigh, Champion Park, Denmark Hill, S.E.,
November 1.

It appears to me that Prof. Kipping and Mr. Pope unintentionally attribute to me opinions which I have never expressed, and which I do not hold. I never for a moment imagined that in each separate crystallisation—either of molecularly symmetric substances which, like sodium chlorate, may form either right-handed or left-handed crystals, or of the externally compensated mixture of dextro- and laevo-rotatory sodium ammonium tartrates, in which the asymmetry is molecular—equal amounts of the two kinds of crystals would necessarily be deposited. I never thought of this equality as holding good, except as the mean of a great number of experiments. In my address, when referring to Messrs. Kipping and Pope's results obtained with sodium chlorate, I therefore used the expression "on the average." Besides, I was acquainted with Landolt's experiments on the subject, which prove the same thing. In the case of the dextro- and laevo-rotatory sodium ammonium tartrates, the Pasteur-Gernez method of separating these by starting the crystallisation with a crystal of one of the two kinds, and Jungfleisch's experiments, to which I will refer more fully later on, were sufficient to make me aware of the influence of initial bias on crystallisation, and to prevent me from expecting equality, except as a mean result.

In fact, in these crystallisations everything depends on this initial bias; and in this respect, Landolt's experiments are especially instructive. His method (*Ber. d. deutsch. chem. Ges.*, 1896, p. 2410) consists in precipitating aqueous solutions of sodium chlorate by addition of alcohol. A magma of minute crystals is thus obtained, each of which must be either right-handed or left-handed. The crystals are then filtered off and ground to a fine powder; and this powder, suspended in a mixture of alcohol and carbon disulphide, is examined in the polarimeter. If both enantiomorphous forms are present in equal quantity, there will be no rotatory effect; whereas a preponderance of either form will be indicated by a rotation in the corresponding sense.

Landolt found that if the precipitation was rapidly effected by the sudden addition of alcohol, the powder was either inactive, or had a very feeble rotation. On the other hand, if the alcohol was gradually added, so as to produce slow precipitation, the powder displayed a marked rotation, which was in some cases right-handed, in others left-handed. The reason is obvious. In the former case, the crystallisation starts simultaneously from a vast number of independent centres; the chances are equal in favour of each centre being right-handed or left-handed; each centre will propagate its own kind; and thus the ratio of right-handed to left-handed forms will not differ very appreciably from unity. In the latter case, as Landolt points out, the crystallisation starts from only a few centres; in these, therefore, either the right-handed or the left-handed form may predominate, and, as sufficient time is given, the dominant form will influence the course of the crystallisation.

In Messrs. Kipping and Pope's slow crystallisations, every opportunity is afforded for any initial asymmetric bias to exercise its influence; and I should have been greatly surprised if the authors had obtained a result other than that which they describe.

There is, therefore, a marked difference between the formation of enantiomorphous crystals and of enantiomorphous molecules respectively, *under symmetric conditions*: namely, that the crystals propagate their own asymmetry, whilst the molecules, as I pointed out in my reply to Prof. Karl Pearson, do not—at least, so far as experiment informs us.

In the crystallisation of the externally compensated mixture of dextro- and laevo-rotatory sodium ammonium tartrates, one would expect a similar state of things to prevail, modified however by the circumstance that in this case the two opposite asymmetries of the molecules themselves are pre-existent in the solution and must influence the result. One would expect variations, within limits, of the relative quantities of dextro- and laevo-salts deposited; but according to our present views, *the mean variation should occur equally in opposite directions*.

It is therefore with great surprise that I learn that in the ten experiments which Messrs. Kipping and Pope have hitherto made on this point they obtained in every case a strongly dextro-rotatory deposit. It is true that Jungfleisch (compare *Chem. News*, vol. 40, p. 231) published, in 1884, similar results. Jungfleisch's procedure was somewhat different from that of Messrs. Kipping and Pope. Instead of allowing the solution to crystallise spontaneously, he introduced simultaneously into the supersaturated solution, at opposite sides of the crystallising dish, a crystal of the dextro-rotatory and one of the laevo-rotatory salt. In all his experiments the former crystal showed the greater increase in weight, and the mother liquor contained a corresponding excess of the laevo-salt. I confess that I have always attributed Jungfleisch's results to mere coincidence. It will doubtless be within Prof. Kipping's recollection that in April last I wrote to him calling his attention to these results, in connection with his joint work with Mr. Pope. Prof. Kipping replied (I quote from memory), that Jungfleisch's results were opposed to all that was known of the behaviour of enantiomorphs; that he (Prof. Kipping) did not regard them as conclusive; and that he proposed to repeat them. This he and Mr. Pope have now done; but from what I have just said, it is evident that the outcome of this repetition must have been as great a surprise to him as it is to me. I am glad to find, however, that the authors put forward their results with reserve, and that they contemplate the possibility of discovering some disturbing influence. If no such influence is at work, it is not merely the small matter of my particular application of the principles of molecular asymmetry that will have to go: it is these principles themselves. But I do not anticipate any such catastrophe. The vast accumulation of verified prediction of which the science of stereochemistry can boast, does not point to premises so unsound.

I will wait, therefore, for further light on Messrs. Kipping and Pope's later experiments before drawing any conclusion from them. As regards the experiments with sodium chlorate, I am at a loss to understand in what way they militate against my views. I no more expect equal numbers of right and left crystals to separate in any given crystallisation of sodium chlorate than I expect an unvarying alternation of heads and tails in tossing a coin. Nor do I perceive the application of the experiment in which they obtained none but right-handed crystals of the chlorate; inasmuch as, if they go on repeating it, they will obtain, just as often, none but left-handed crystals. The process will not *constantly* yield the same form.

I must also repeat that I do not regard the spontaneous formation of "optically active mother liquors," or other partial separations of enantiomorphs, especially when the separation may occur in either direction, as a solution of the problem. The separation of enantiomorphs in the living world is, in the overwhelming majority of cases, as I have pointed out in a previous reply, not partial but *total*; and it occurs *constantly* in one direction—only one form survives. This is another case where the word "constantly" applies—a word quoted by the authors, but otherwise ignored by them, except where they are discussing experiments which they themselves regard as requiring confirmation.

I think, moreover, that my critics might in justice take into account the disadvantage under which I laboured in having to compress into the limits of a brief address an account of a subject so vast and intricate. Many of my statements on important points were necessarily somewhat summary and inadequate; and most of the misunderstandings into which my various critics have fallen are, I am aware, due to this circumstance.

The University, Aberdeen, November 10. F. R. JAPP.